

UNITED STATES PATENT AND TRADEMARK OFFICE

I, Charles Edward SITCH BA,

Deputy Managing Director of RWS Group plc, of Europa House, Marsham Way, Gerrards Cross, Buckinghamshire, England declare;

1. That I am a citizen of the United Kingdom of Great Britain and Northern Ireland.
2. That the translator responsible for the attached translation is well acquainted with the German and English languages.
3. That the attached is, to the best of RWS Group plc knowledge and belief, a true translation into the English language of the accompanying copy of the specification filed with the application for a patent in Germany on 13 June 1994 under the number P 44 20 456.6 and the official certificate attached hereto.
4. That I believe that all statements made herein of my own knowledge are true and that all statements made on information and belief are true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the patent application in the United States of America or any patent issuing thereon.



For and on behalf of RWS Group plc

The 12th day of February 2004

HOECHST AKTIENGESELLSCHAFT HOE 94/F 160 Dr. SK/do

Description

5 Transition metal compound

The present invention relates to a zwitterionic transition metal compound which can be advantageously used for the polymerization of olefins. In this way, the use of
10 aluminoxanes such as methylaluminoxane (MAO) as cocatalyst can be omitted while still achieving high catalyst activities.

The role of cationic 14-electron complexes of the form
15 R_3M^+ ($M = Ti, Zr, Hf$) in Ziegler-Natta polymerization using metallocenes is generally recognized (M. Bochmann, Nachr. Chem. Lab. Techn. 1993, 41, 1220).

While MAO, as the hitherto most effective cocatalyst,
20 has to be used in a high excess, the synthesis of cationic alkyl complexes of the form R_3M^+ ($M = Ti, Zr, Hf$) provides a route to MAO-free catalysts, some of which have comparable activity.

25 Cationic alkyl complexes can be prepared by

- a) oxidation of metallocene-dialkyl complexes with, for example, $AgBPh_4$ or $[Cp_2Fe][BPh_4]$,
- b) by protolysis of metallocene-alkyl compounds with, for example, weakly acid ammonium salts of the very
30 stable, nonbasic tetra(pentafluorophenyl)borate anion (e.g. $[PhMe_2NH]^+[B(C_6F_5)_4]^-$) or by
- c) abstraction of an alkyl group from metallocene-alkyl compounds by means of strong Lewis acids.
35 Lewis acids which can be used here are salts $(Ph_3C^+BR_4^-)$ or strong neutral Lewis acids such as $B(C_6F_5)_3$.

J. Organomet. Chem. 1970, 22, 659, describes a reaction of tetramethyltitanium with triphenylborane or

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tribenzylborane.

J. Am. Chem. Soc. 1991, 113, 3623, describes the synthesis of "cation-like" metallocene polymerization catalysts which are prepared by alkyl abstraction from metallocene-alkyl compounds using tris(pentafluorophenyl)borane. The crystal structure of $[1,2-(CH_3)_2C_5H_3]_2-ZrCH_3]^+[CH_3B(C_6F_5)_3]^-$ shows a salt-like structure with weak coordination of the CH_3 group of the borate anion to the metal center. EP 427,697 claims this synthetic principle and a corresponding catalyst system comprising a neutral metallocene species (eg. Cp_2ZrMe_2), a Lewis acid (eg. $B(C_6F_5)_3$) and aluminum alkyls. EP 520,732 claims a process for preparing salts of the form LMX^+XA^- according to the abovedescribed principle.

EP 558,158 claims zwitterionic catalyst systems prepared from metallocene-dialkyl compounds and salts of the form $[R_3NH]^+[BPh_4]^-$. Reaction of such a salt with $Cp^*_2ZrMe_2$ generates, by means of protolysis with elimination of methane, an intermediate zirconocene-methyl cation which reacts, after C-H activation of a tetraphenylborate carbon-hydrogen bond and renewed elimination of methane, to give the zwitterion $Cp^*_2Zr^+-(m-C_6H_4)-B^-Ph_3$. The Zr atom is here covalently bonded to a carbon atom of the phenyl ring and is stabilized via an agostic hydrogen bond. According to this reaction principle, protolysis of a metallocene-dialkyl species with a perfluorinated $[R_3NH]^+[B(C_6F_5)_4]^-$ salt in the first step likewise forms a cationic species, with the subsequent reaction (C-H activation) to give zwitterionic complexes (i.e. the metal atom is covalently bonded to the "former" anion) not being possible. This process also uses metallocenes Cp_2MR_2 in which the alkyl radicals R are cyclically bonded to one another, for example $Cp_2Zr(2,3\text{-dimethyl-1,3-butadiene})$. Salts of the form $[Cp_2Zr-R-RH]^+[B(C_6F_5)_4]^-$ are formed after protonolysis.

US 5,198,401 claims corresponding systems in which

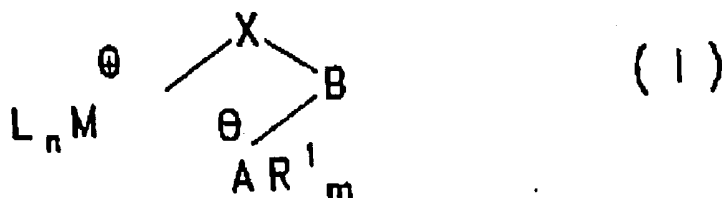
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- dimethylanilinium salts having perfluorinated tetraphenylborate anions are used. This reference also uses metallocenes Cp_2MR_2 in which the alkyl radicals R are cyclically bonded to one another, for example Cp_2Zr -
5 (2,3-dimethyl-1,3-butadiene). After protonolysis, salts of the form $[\text{Cp}_2\text{Zr-R-RH}]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ are likewise formed. EP 277,003, EP 277,004, EP 495,375 and WO 91/14713 claim systems according to a similar process principle.
- 10 The processes described for preparing the cationic systems of the form $[\text{R}_3\text{M}]^+[\text{BR}_4]^-$ (M = Ti, Zr, Hf) have the disadvantage that the cationizing reagents ($\text{R}_3\text{NH}^+\text{BR}_4^-$) are sometimes complicated to synthesize and
15 R_3N is formed from the ammonium salt after protonolysis, which amine, in the case of sterically unhindered metal centers, can coordinate to the strong Lewis acid R_3M^+ cation (US 5,198,401) and thus leads to low polymerization activities.
- 20 The zwitterionic complexes of the structure $\text{Cp}_2\text{Zr}^+-m-\text{C}_6\text{H}_4\text{B}^-\text{Ph}_3$ have the disadvantage that the starting compounds are expensive and complicated to synthesize and have low polymerization activity.
- 25 Owing to their salt-like character, cationic systems of the structure $[\text{Cp}_2\text{MR}]^+[\text{RB}(\text{C}_6\text{F}_5)_3]^-$ have very high hydrolysis sensitivities and can be used on an industrial scale only to a limited extent. The activities observed for
30 these systems are low owing to the abovementioned stability problems and the presumably sometimes strong coordination of the alkyl group of the borate anion to the metal center.
- 35 It is an object of the invention to find a catalyst system which avoids the disadvantages of the prior art.

It has now been found that this object can be achieved by specific zwitterionic transition metal compounds.

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The present invention accordingly provides a zwitterionic transition metal compound of the formula I



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where

- 10 L are identical or different and are each a π ligand or an electron donor, where two radicals L can be linked to one another via a bridge Z, n is equal to 1, 2, 3 or 4,
- M is a metal of group IIb, IVb, Vb or VIb of the Periodic Table of the Elements,
- 15 X is a heteroatom or a hydrocarbon group,
- B is a hydrocarbon group,
- 20 A is a metal atom of group Ib, IIb, IIIa, IIIb, IVa, Va, Vb, VIb, VIIb or VIIIb,
- R¹ are identical or different and are each a perhalogenated hydrocarbon radical, and m is equal to 1, 2, 3, 4 or 5,
- where if M is a metal of group IVb, n is 2.

25 The metal atoms M and A are covalently bonded to one another via the structural elements X and B, where if X is an allyl unit, the bonding of X to the metal M can be a σ -allyl or a π -allyl bond.

30 π Ligands are preferably unsubstituted or substituted cyclopentadienyl groups such as 2-methylcyclopentadienyl, indenyl, 2-methyl-4-phenylindenyl, 4,5-benzoindenyl, fluorenyl or 4,7-tert-butylfluorenyl.

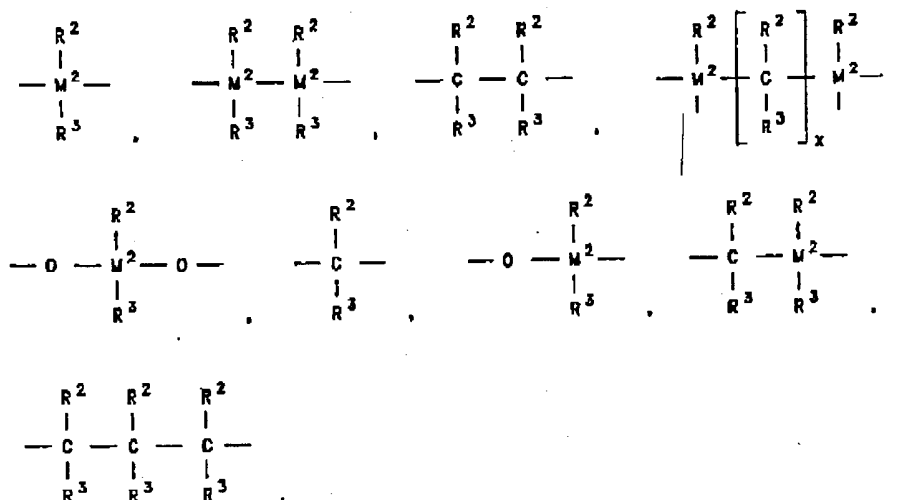
For the purposes of the present invention, an electron donor is an atom of group IVa, Va, VIa or VIIa of the

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Periodic Table of the Elements, which can bear substituents such as hydrocarbon groups. Preference is given to O, NR^4_2 , NR^4 , NR^4_3 , PR^4_2 , PR^4 , PR^4_3 , S, $\text{P(OR}^4)_2$, $\text{P(OR}^4)$, R^4 or Cl, where R^4 is C_1 - C_{20} -alkyl or C_6 - C_{14} -aryl.

5

The bridge Z is preferably



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$=\text{BR}^2$, $-\text{AlR}^2$, $-\text{Ge}-$, $-\text{O}-$, $-\text{S}-$, $=\text{SO}$, $=\text{SO}_2$, $-\text{NR}^2$, $=\text{CO}$, $=\text{PR}^2$ or $=\text{P(O)R}^2$, where R^2 and R^3 are identical or different and are each a hydrogen atom, a halogen atom, a C_1 - C_{20} -alkyl group, a C_1 - C_{10} -fluoroalkyl group, a C_1 - C_{10} -alkoxy group, a C_6 - C_{14} -aryl group, a C_6 - C_{10} -fluoroaryl group, a C_6 - C_{10} -aryloxy group, a C_2 - C_{10} -alkenyl group, a C_7 - C_{40} -arylalkyl group, a C_7 - C_{40} -alkylaryl group, a C_8 - C_{40} -arylalkenyl group and x is a number from zero to 18, or R^2 and R^3 together with the atoms connecting them form one or more

20 rings and

R^2 or/and R^3 can be bonded to L and

M^2 is silicon, germanium or tin.

Z can also link two groups $\text{L}_m\text{M}^*\text{XBA}^*\text{R}^1_m$ with one another.

25 For the purposes of the present invention, a heteroatom is any atom of the Periodic Table of the Elements with the exceptions of carbon and hydrogen. Preference is

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given to O, S and N.

The hydrocarbon groups can be saturated or unsaturated, linear or branched, eg. a C_1 - C_{20} -alkyl group, a C_6 - C_{14} -aryl group, a C_2 - C_{10} -alkenyl group, a C_7 - C_{40} -arylalkyl group, a C_7 - C_{40} -alkylaryl group or a C_8 - C_{40} -arylalkenyl group. Preference is given to substituted or unsubstituted alkyl groups which can also have aromatic structural elements.

10

Preference is given to $n = 1$ when M is an element of group IIb; $n = 3$ when M is an element of group Vb; and $n = 4$ when M is an element of group VIb.

15 Particular preference is given to compounds of the formula I, where

M is titanium, zirconium, hafnium or vanadium,

n is equal to 2,

20 L are identical or different and are each a substituted or unsubstituted cyclopentadienyl group, where two radicals L can be linked to one another via a bridge Z, where

Z can be CR^2R^3 or SiR^2R^3 or is a unit $Si-(CR^2R^3)_x-Si$ which links two fragments $L_nM^+-X-B-A-R_m^1$ with one another, where x is from 0 to 10, preferably $x = 6$.

25

X and B together form a three-membered to five-membered alkyl chain which can be saturated or unsaturated and substituted by hydrocarbon radicals,

A is a metal of group Ib, IIb, IIIa, IVa, Va, Vb,

30 R^1 are identical or different and are each a perfluorinated alkyl or aryl group and

m is equal to 2, 3 or 4.

35 Very particular preference is given to compounds of the formula I, where

M is zirconium,

n is equal to 2,

L are identical or different and are each a substituted cyclopentadienyl group, where two radicals L

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are bonded to one another via a bridge Z, where Z is a substituted carbon or silicon atom,

X and B together form an unsaturated four-membered alkyl chain whose hydrogen atoms can also be replaced by alkyl groups,

A is a boron atom,

R¹ are identical and are each a pentafluorophenyl group (C₆F₅) and

m is equal to 3.

Examples of compounds of the invention are:

bis(cyclopentadienyl)Zr⁺CH₂CHCHCH₂B⁻(C₆F₅)₃;

bis(methylcyclopentadienyl)Zr⁺CH₂CHCHCH₂B⁻(C₆F₅)₃;

bis(n-butylcyclopentadienyl)Zr⁺CH₂CHCHCH₂B⁻(C₆F₅)₃;

bis(indenyl)Zr⁺CH₂CHCHCH₂B⁻(C₆F₅)₃;

(tert-butylamido)dimethyl(tetramethyl-η⁵-cyclopentadienyl)silaneZr⁺CH₂CHCHCH₂B⁻(C₆F₅)₃;

bis(2-methylbenzoindenyl)Zr⁺CH₂CHCHCH₂B⁻(C₆F₅)₃;

dimethylsilanediylbis(2-methylindenyl)Zr⁺CH₂CHCHCH₂B⁻(C₆F₅)₃;

dimethylsilanediylbis(indenyl)Zr⁺CH₂CHCHCH₂B⁻(C₆F₅)₃;

dimethylsilanediylbis(2-methylbenzoindenyl)-

Zr⁺CH₂CHCHCH₂B⁻(C₆F₅)₃;

dimethylsilanediyl(2-methylbenzoindenyl)(2-methylindenyl)Zr⁺CH₂CHCHCH₂B⁻(C₆F₅)₃;

dimethylsilanediyl(2-methylbenzoindenyl)(2-methyl-

4-phenylindenyl)Zr⁺CH₂CHCHCH₂B⁻(C₆F₅)₃;

dimethylsilanediyl(2-methylindenyl)(4-phenylindenyl)-

Zr⁺CH₂CHCHCH₂B⁻(C₆F₅)₃;

dimethylsilanediylbis(2-methyl-4-phenylindenyl)-

Zr⁺CH₂CHCHCH₂B⁻(C₆F₅)₃;

dimethylsilanediylbis(2-methyl-4,6-diisopropylindenyl)-

Zr⁺CH₂CHCHCH₂B⁻(C₆F₅)₃;

dimethylsilanediylbis(2-methyl-4-naphthylindenyl)-

Zr⁺CH₂CHCHCH₂B⁻(C₆F₅)₃;

isopropylidene(cyclopentadienyl)(fluorenyl)-

Zr⁺CH₂CHCHCH₂B⁻(C₆F₅)₃;

isopropylidene(cyclopentadienyl)(indenyl)Zr⁺CH₂CHCHCH₂B⁻-

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- (C₆F₅)₃;
[4-η⁵-cyclopentadienyl)-4,7,7-trimethyl-(η⁵-4,5,6,7-tetrahydroindenyl) Zr⁺CH₂CHCHCH₂B⁻(C₆F₅)₃;
dimethylsilanediylbis(2-methylindenyl) Zr⁺OCH₂CH₂CH₂B⁻(C₆F₅)₃;
5 dimethylsilanediylbisindenyl Zr⁺OCH₂CH₂CH₂B⁻(C₆F₅)₃;
dimethylsilanediylbis(2-methylbenzoindenyl) Zr⁺OCH₂CH₂CH₂B⁻(C₆F₅)₃;
dimethylsilanediyl(2-methylbenzoindenyl)(2-methylindenyl) Zr⁺OCH₂CH₂CH₂B⁻(C₆F₅)₃;
10 dimethylsilanediyl(2-methylbenzoindenyl)(2-methyl-4-phenylindenyl) Zr⁺OCH₂CH₂CH₂B⁻(C₆F₅)₃;
dimethylsilanediyl(2-methylindenyl)(4-phenylindenyl) Zr⁺OCH₂CH₂CH₂B⁻(C₆F₅)₃;
15 dimethylsilanediylbis(2-methyl-4-phenylindenyl) Zr⁺OCH₂CH₂CH₂B⁻(C₆F₅)₃;
dimethylsilanediylbis(2-methyl-4,6-diisopropylindenyl) Zr⁺OCH₂CH₂CH₂B⁻(C₆F₅)₃;
20 dimethylsilanediylbis(2-methylindenyl) Zr⁺CH₂CHCHCH₂B⁻(CF₃)₃;
dimethylsilanediylbisindenyl Zr⁺CH₂CHCHCH₂B⁻(CF₃)₃;
dimethylsilanediylbis(2-methylbenzoindenyl) Zr⁺CH₂CHCHCH₂B⁻(CF₃)₃;
25 dimethylsilanediyl(2-methylbenzoindenyl)(2-methylindenyl) Zr⁺CH₂CHCHCH₂B⁻(CF₃)₃;
dimethylsilanediyl(2-methylbenzoindenyl)(2-methyl-4-phenylindenyl) Zr⁺CH₂CHCHCH₂B⁻(CF₃)₃;
dimethylsilanediyl(2-methylindenyl)(4-phenylindenyl) Zr⁺CH₂CHCHCH₂B⁻(CF₃)₃;
30 dimethylsilanediylbis(2-methyl-4-phenylindenyl) Zr⁺CH₂CHCHCH₂B⁻(CF₃)₃;
dimethylsilanediylbis(2-methyl-4,6-diisopropylindenyl) Zr⁺CH₂CHCHCH₂B⁻(CF₃)₃;
35 dimethylsilanediylbis(2-methyl-4-naphthylindenyl) Zr⁺CH₂CHCHCH₂B⁻(CF₃)₃;

dimethylsilanediylbis(2-methylindenyl) Zr⁺CH₂C(CH₃)C(CH₃)CH₂B⁻(CF₃)₃;

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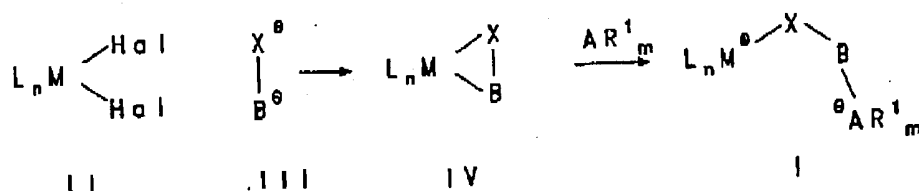
- dimethylsilanediylbisindenylZr⁺CH₂C(CH₃)C(CH₃)CH₂B⁻(CF₃)₃;
 dimethylsilanediylbis(2-methylbenzoindenyl)Zr⁺CH₂C(CH₃)C-
 (CH₃)CH₂B⁻(CF₃)₃;
 dimethylsilanediyl(2-methylbenzoindenyl)(2-methyl-
 5 indenyl)Zr⁺CH₂C(CH₃)C(CH₃)CH₂B⁻(CF₃)₃;
 dimethylsilanediyl(2-methylbenzoindenyl)(2-methyl-
 4-phenylindenyl)Zr⁺CH₂C(CH₃)C(CH₃)CH₂B⁻(CF₃)₃;
 dimethylsilanediyl(2-methylindenyl)(4-phenylindenyl)-
 Zr⁺CH₂C(CH₃)C(CH₃)CH₂B⁻(CF₃)₃;
 10 dimethylsilanediylbis(2-methyl-4-phenylindenyl)Zr⁺CH₂-
 C(CH₃)C(CH₃)CH₂B⁻(CF₃)₃;
 dimethylsilanediylbis(2-methyl-4,6-diisopropylindenyl)-
 Zr⁺CH₂C(CH₃)C(CH₃)CH₂B⁻(CF₃)₃;
 dimethylsilanediylbis(2-methyl-4-naphthylindenyl)Zr⁺CH₂-
 15 C(CH₃)C(CH₃)CH₂B⁻(CF₃)₃;
 methylphenylmethylene(fluorenyl)(cyclopentadienyl)-
 Zr⁺CH₂CHCHCH₂B⁻(C₆F₅)₃;
 diphenylmethylene(fluorenyl)(cyclopentadienyl)-
 Zr⁺CH₂CHCHCH₂B⁻(C₆F₅)₃;
 20 isopropylidene(3-methylcyclopentadienyl)(fluorenyl)-
 Zr⁺CH₂CHCHCH₂B⁻(C₆F₅)₃;
 dimethylsilanediyl(3-tert-butylcyclopentadienyl)-
 (fluorenyl)Zr⁺CH₂CHCHCH₂B⁻(C₆F₅)₃;
 diphenylsilanediyl(3-(trimethylsilyl)cyclopentadienyl)-
 25 (fluorenyl)Zr⁺CH₂CHCHCH₂B⁻(C₆F₅)₃;
 phenylmethylsilanediylbis(2-methylindenyl)Zr⁺CH₂CHCHCH₂B⁻
 (C₆F₅)₃;
 phenylmethylsilanediylbisindenylZr⁺CH₂CHCHCH₂B⁻(C₆F₅)₃;
 phenylmethylsilanediylbis(2-methyl-4,5-benzoindenyl)-
 30 Zr⁺CH₂CHCHCH₂B⁻(C₆F₅)₃;
 phenylmethylsilanediyl(2-methyl-4,5-benzoindenyl)-
 (2-methylindenyl)Zr⁺CH₂CHCHCH₂B⁻(C₆F₅)₃;
 phenylmethylsilanediyl(2-methyl-4,5-benzoindenyl)-
 (2-methyl-4-phenylindenyl)Zr⁺CH₂CHCHCH₂B⁻(C₆F₅)₃;
 35 phenylmethylsilanediyl(2-methylindenyl)(4-phenylindenyl)
 Zr⁺CH₂CHCHCH₂B⁻(C₆F₅)₃;
 phenylmethylsilanediylbis(2-methyl-4-phenylindenyl)-
 Zr⁺CH₂CHCHCH₂B⁻(C₆F₅)₃;
 phenylmethylsilanediylbis(2-ethyl-4-phenylindenyl)-

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- $\text{Zr}^+\text{CH}_2\text{CHCHCH}_2\text{B}^-(\text{C}_6\text{F}_5)_3$;
 phenylmethylsilanediylbis(2-methyl-4,6-diisopropyl-
 indenyl) $\text{Zr}^+\text{CH}_2\text{CHCHCH}_2\text{B}^-(\text{C}_6\text{F}_5)_3$;
 phenylmethylsilanediylbis(2-methyl-4-naphthylindenyl)-
 5 $\text{Zr}^+\text{CH}_2\text{CHCHCH}_2\text{B}^-(\text{C}_6\text{F}_5)_3$;
 ethylenebis(2-methylindenyl) $\text{Zr}^+\text{CH}_2\text{CHCHCH}_2\text{B}^-(\text{C}_6\text{F}_5)_3$;
 ethylenebisindenyl $\text{Zr}^+\text{CH}_2\text{CHCHCH}_2\text{B}^-(\text{C}_6\text{F}_5)_3$;
 ethylenebis(2-methyl-4,5-benzoindenyl) $\text{Zr}^+\text{CH}_2\text{CHCHCH}_2\text{B}^-(\text{C}_6\text{F}_5)_3$;
 10 ethylene(2-methyl-4,5-benzoindenyl)(2-methylindenyl)-
 $\text{Zr}^+\text{CH}_2\text{CHCHCH}_2\text{B}^-(\text{C}_6\text{F}_5)_3$;
 ethylene(2-methyl-4,5-benzoindenyl)(2-methyl-4-phenyl-
 indenyl) $\text{Zr}^+\text{CH}_2\text{CHCHCH}_2\text{B}^-(\text{C}_6\text{F}_5)_3$;
 ethylene(2-methylindenyl)(4-phenylindenyl) $\text{Zr}^+\text{CH}_2\text{CHCH}-$
 15 $\text{CH}_2\text{B}^-(\text{C}_6\text{F}_5)_3$;
 ethylenebis(2-methyl-4,5-benzoindenyl) $\text{Zr}^+\text{CH}_2\text{CHCHCH}_2\text{B}^-(\text{C}_6\text{F}_5)_3$;
 ethylenebis(2-methyl-4-phenylindenyl) $\text{Zr}^+\text{CH}_2\text{CHCHCH}_2\text{B}^-(\text{C}_6\text{F}_5)_3$;
 20 ethylenebis(2-methyl-4,6-diisopropylindenyl) $\text{Zr}^+\text{CH}_2\text{CHCH}-$
 $\text{CH}_2\text{B}^-(\text{C}_6\text{F}_5)_3$;
 ethylenebis(2-methyl-4-naphthylindenyl) $\text{Zr}^+\text{CH}_2\text{CHCHCH}_2\text{B}^-(\text{C}_6\text{F}_5)_3$;
 ethylenebis(2-ethyl-4-phenylindenyl) $\text{Zr}^+\text{CH}_2\text{CHCHCH}_2\text{B}^-(\text{C}_6\text{F}_5)_3$;
 25 ethylenebis(2-ethyl-4,6-diisopropylindenyl) $\text{Zr}^+\text{CH}_2\text{CHCH}-$
 $\text{CH}_2\text{B}^-(\text{C}_6\text{F}_5)_3$;
 ethylenebis(2-ethyl-4-naphthylindenyl) $\text{Zr}^+\text{CH}_2\text{CHCHCH}_2\text{B}^-(\text{C}_6\text{F}_5)_3$;
 dimethylsilanediylbis(2-ethyl-4-phenylindenyl) $\text{Zr}^+\text{CH}_2\text{CHCH}-$
 30 $\text{CH}_2\text{B}^-(\text{C}_6\text{F}_5)_3$;
 dimethylsilanediylbis(2,3,5-trimethylcyclopentadienyl)-
 $\text{Zr}^+\text{CH}_2\text{CHCHCH}_2\text{B}^-(\text{C}_6\text{F}_5)_3$;
 1,6-{bis[methylsilylbis(2-methyl-4-phenylindenyl)-
 $\text{Zr}^+\text{CH}_2\text{CHCHCH}_2\text{B}^-(\text{C}_6\text{F}_5)_3$]}hexane;
 35 1,6-{bis[methylsilylbis(2-ethyl-4-phenylindenyl) $\text{Zr}^+\text{CH}_2\text{CH}-$
 $\text{CHCH}_2\text{B}^-(\text{C}_6\text{F}_5)_3$]}hexane;
 1,6-{bis[methylsilylbis(2-methyl-4-naphthylindenyl)-
 $\text{Zr}^+\text{CH}_2\text{CHCHCH}_2\text{B}^-(\text{C}_6\text{F}_5)_3$]}hexane;
 1,6-{bis[methylsilylbis(2-methyl-4,5-benzoindenyl)-

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- $\text{Zr}^+\text{CH}_2\text{CHCHCH}_2\text{B}^-(\text{C}_6\text{F}_5)_3\}$ hexane;
 1,6-{bis[methylsilyl(2-methyl-4-phenylindenyl)(2-methyl-
 indenyl)] $\text{Zr}^+\text{CH}_2\text{CHCHCH}_2\text{B}^-(\text{C}_6\text{F}_5)_3\}$ hexane;
 1,2-{bis[methylsilylbis(2-methyl-4-phenylindenyl)-
 5 $\text{Zr}^+\text{CH}_2\text{CHCHCH}_2\text{B}^-(\text{C}_6\text{F}_5)_3\}$ ethane;
 1,2-{bis[methylsilylbis(2-ethyl-4-phenylindenyl)] $\text{Zr}^+\text{CH}_2\text{CH}-$
 $\text{CHCH}_2\text{B}^-(\text{C}_6\text{F}_5)_3\}$ ethane;
 1,2-{bis[methylsilylbis(2-methyl-4-naphthylindenyl)-
 $\text{Zr}^+\text{CH}_2\text{CHCHCH}_2\text{B}^-(\text{C}_6\text{F}_5)_3\}$ ethane;
 10 1,2-{bis[methylsilylbis(2-methyl-4,5-benzoinindenyl)-
 $\text{Zr}^+\text{CH}_2\text{CHCHCH}_2\text{B}^-(\text{C}_6\text{F}_5)_3\}$ ethane;
 1,2-{bis[methylsilyl(2-methyl-4-phenylindenyl)(2-methyl-
 indenyl)] $\text{Zr}^+\text{CH}_2\text{CHCHCH}_2\text{B}^-(\text{C}_6\text{F}_5)_3\}$ ethane.
- 15 The preparation of the novel transition metal compound
 of the formula I is illustrated by the following
 reaction schemes.



- 20 L, n, M, X, B, A, R¹ and m in the formulae II, III and
 IV are as defined in formula I and Hal is a halogen such
 as chlorine.
- Compounds of the formula II are described many times in
 25 the literature (J. Okuda, Topics in Current Chemistry,
 Vol. 160; Springer Verlag, Berlin Heidelberg 1991, page
 97). Reaction of compounds of the formula II in inert
 solvents with dianion compounds of the formula III, for
 example 1,4-butanediyl lithium or 2-butene-
 30 1,4-diylmagnesium, leads to elimination of a salt and
 formation of the cyclic systems IV in which the M-X or
 M-B bond can be a covalent bond or a coordination of an
 olefin to the metal.

- 12 -

The compounds of the formula IV are reacted with Lewis acids of the form AR_m^1 in organic solvents, for example toluene, benzene, methylene chloride, carbon tetrachloride and petroleum spirit.

5

The novel catalyst systems of the formula I can be isolated or directly used for further reactions. The systems of the formula I can also be prepared without isolation of intermediate and end stages in a single-vessel reaction from metallocene dihalides, dianion compounds and Lewis acids and be directly used for the polymerization.

15 Suitable solvents are aliphatic or aromatic solvents, such as hexane or toluene, or halogenated hydrocarbons, such as methylene chloride, or halogenated aromatic hydrocarbons such as o-dichlorobenzene.

20 A further possibility for preparing the novel compounds comprises formation of metallocycles of the formula IV by electrocyclic ring-closure reaction of, for example, metallocene-bisolefin complexes or metallocene-olefin-aldehyde complexes.

25 The present invention also relates to a process for preparing an olefin polymer by polymerization or copolymerization of at least one olefin in the presence of a catalyst containing at least one transition metal compound of the formula I.

30

Preference is given to polymerizing or copolymerizing olefins of the formula $R^a-CH=CH-R^b$, where R^a and R^b are identical or different and are each a hydrogen atom, a halogen atom, an alkoxy group, a hydroxy group, an alkylhydroxy group, an aldehyde group, a carboxylic acid group or a carboxylic ester group or a hydrocarbon radical having from 1 to 20 carbon atoms, in particular from 1 to 10 carbon atoms, which can be substituted by an alkoxy group, a hydroxy group, an alkylhydroxy group,

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an aldehyde group, a carboxylic acid group or a carboxylic ester group, or R^a and R^b together with the atoms connecting them can form a one or more rings. Examples of such olefins are ethylene, propylene, 1-butene, 1-hexene, 4-methyl-1-pentene, 1-octene, norbornene, vinylnorbornene, tetracyclododecene, ethylidenenorbornene, bicyclopentadiene, methyl methacrylate. In particular, propylene or ethylene are polymerized, or else norbornene and ethylene are copolymerized.

The polymerization or copolymerization is preferably carried out at a temperature of from -60 to 300°C , particularly preferably from 30 to 250°C . The pressure is from 0.5 to 2500 bar, preferably from 2 to 1500 bar. The polymerization can be carried out continuously or batchwise, in one or more stages, in solution, in suspension, in the gas phase or in a supercritical medium.

The compounds of the invention are highly active catalyst components for olefin polymerization.

It is also possible to use mixtures of two or more metallocenes. By this means, polyolefins having a broad or multimodal molecular weight distribution can be obtained.

A prepolymerization can be carried out by means of the metallocene. For the prepolymerization, preference is given to using the (or one of the) olefin(s) used in the polymerization.

The compounds of the formula I can also be applied to a support. Suitable support materials are, for example, silica gels, aluminum oxides, solid aluminosilicate or other inorganic support materials such as, for example, magnesium chloride. Another suitable support material is a polyolefin powder in finely divided form.

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The supported catalyst system can be resuspended as powder or still together with solvent and can be metered into the polymerization system as a suspension in an inert suspension medium.

To remove catalyst poisons present in the olefin, purification using an aluminum alkyl, for example trimethylaluminum or triethylaluminum, is advantageous.

10 This purification can be carried out either in the polymerization system itself or the olefin is contacted with the Al compound and subsequently separated again prior to its addition to the polymerization system.

15 Hydrogen is added, if required, as molecular weight regulator and/or to increase the activity. The total pressure in the polymerization system is from 0.5 to 2500 bar, preferably from 2 to 1500 bar.

20 The metallocene is here used in a concentration, based on the transition metal, of preferably from 10^{-3} to 10^{-8} , particularly preferably from 10^{-4} to 10^{-7} , mol of transition metal per dm^3 of solvent or per dm^3 of reactor volume.

25

If the polymerization is carried out as a suspension or solution polymerization, an inert solvent customary for the Ziegler low-pressure process is used. For example, the polymerization is carried out in an aliphatic or cycloaliphatic hydrocarbon; examples of such solvents which may be mentioned are propane, butane, hexane, heptane, isooctane, cyclohexane, methylcyclohexane. Furthermore, a petroleum or hydrogenated diesel oil fraction can be used. It is also possible to use

30 toluene. Preference is given to carrying out the polymerization in the liquid monomer.

35

If inert solvents are used, the monomers are metered in in gaseous or liquid form.

- 15 -

The duration of the polymerization can be as desired, since the catalyst system to be used according to the invention has only a small fall in polymerization activity with time.

Prior to addition of the catalyst, in particular the supported catalyst system (comprising a metallocene of the invention and a support material or on a polyolefin powder in finely divided form), another aluminum alkyl compound such as, for example, trimethylaluminum, triethylaluminum, triisobutylaluminum, trioctylaluminum or isoprenylaluminum can additionally be added to the reactor to stabilize the polymerization system (for example for removing catalyst poisons present in the olefin). This is added to the polymerization system in a concentration of from 100 to 0.01 mmol of Al per kg of reactor contents. Preference is given to triisobutylaluminum and triethylaluminum in a concentration of from 10 to 0.1 mmol of Al per kg of reactor contents. This enables a small Al/M molar ratio to be selected in the synthesis of a supported catalyst system.

In principle, however, the use of further substances to catalyse the polymerization reaction is not required, i.e. the systems of the invention can be used as sole catalysts for olefin polymerization.

The following examples serve to illustrate the invention.

General procedures: Preparation and handling of organo-metallic compounds were carried out with exclusion of air and moisture under argon protection (Schlenk technique). All solvents required were dried prior to use by boiling for a number of hours over a suitable desiccant and subsequent distillation.

The compounds were characterized using ^1H -NMR, ^{13}C -NMR

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and IR spectroscopy.

A. Synthesis of the compounds of the formula IV

- 5 The preparation of the butadiene complexes was carried out according to G. Erker, K. Engel, Ch. Sarter in R.B. King, J.J. Eisch, Organometallic Synthesis, Vol 3, Academic Press, New York 1986, 529:

10 Example 1:

Dimethylsilanediylbis(2-methyl-4,5-benzoindenyl)-
zirconium(η^4 -butadiene):

- 15 100 ml of toluene (precooled to -40°C) are added to a mixture of 5.0 g (8.67 mmol) of dimethylsilanediyl-(2-methyl-4,5-benzoindenyl)zirconium dichloride and 2.3 g (10.4 mmol, 1.2 equivalents) of (2-butene-1,4-diyl)magnesium bistetrahydrofuran ("butadiene-
20 magnesium") which has been cooled to -40°C . While stirring vigorously, the mixture is allowed slowly to warm up to room temperature. After stirring for four hours, the dark red solution is separated via a frit from unreacted butadienemagnesium and magnesium chloride
25 formed. The filtrate is evaporated to dryness and the residue is washed with 10 ml of pentane. This gives 4.4 g (70%) of a deep red powder.

Example 2:

30

Dimethylsilanediylbis(2-methyl-4-phenylindenyl)-
zirconium(η^4 -butadiene):

- 100 ml of toluene (precooled to -40°C) are added to a
35 mixture of 5.0 g (7.95 mmol) of dimethylsilanediyl-(2-methyl-4-phenylindenyl)zirconium dichloride and 2.1 g (0.95 mmol, 1.2 equivalents) of (2-butene-1,4-diyl)-magnesium bistetrahydrofuran ("butadienemagnesium") which has been cooled to -40°C . While stirring

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vigorously, the mixture is allowed slowly to warm up to room temperature. After stirring for four hours, the dark red solution is separated via a frit from unreacted butadienemagnesium and magnesium chloride formed. The filtrate is evaporated to dryness and the residue is washed with 10 ml of pentane. This gives 3.5 g (72%) of a red-brown powder.

B. Synthesis of the compounds of the formula I:

Example 3:

Dimethylsilanediylbis(2-methyl-4,5-benzoindenyl)-
 $Zr^+CH_2CHCHCH_2B^-(C_6F_5)_3$.

3.0 g (5.35 mmol) of dimethylsilanediyl(2-methyl-4,5-benzoindenyl)zirconium(η^4 -butadiene) are dissolved in 100 ml of toluene and admixed with 3.01 g (5.88 mmol, 1.1 equivalents) of tris(pentafluorophenyl)borane. The reaction solution is left stirring for 24 hours at room temperature and the strongly dark brown suspension is subsequently evaporated to half its volume. The precipitate is filtered off and washed with 10 ml of pentane. This gives 5.27 g (92%) of a sparingly soluble reddish brown powder.

Example 4:

Dimethylsilanediylbis(2-methyl-4-phenylindenyl)-
 $Zr^+CH_2CHCHCH_2B^-(C_6F_5)_3$

3.0 g (4.90 mmol) of dimethylsilanediyl(2-methyl-4-phenylindenyl)zirconium(η^4 -butadiene) are dissolved in 100 ml of toluene and admixed with 2.76 g (5.39 mmol, 1.1 equivalents) of tris(pentafluorophenyl)borane. The reaction solution is left stirring for 24 hours at room temperature and the strongly dark brown suspension is subsequently evaporated to half its volume. The precipitate is filtered off and washed with 10 ml of pentane.

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This gives 4.84 g (88%) of a sparingly soluble reddish brown powder.

C. Polymerization examples

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Example 5:

The catalyst solution is prepared by mixing 11 mg of biscyclopentadienylzirconium(η^4 -butadiene) in 20 ml of
10 toluene with a solution of 20.4 mg of tris(pentafluorophenyl)borane in 20 ml of toluene. 900 ml of toluene are admixed with 1 ml of a 10% strength by weight TIBA solution in toluene and subsequently with 1 ml of this catalyst solution.

15 For the polymerization, this solution is placed in an inert 1.5 dm³ stirred reactor, heated to 70°C and polymerization is carried out at a pressure of 7 bar of ethylene. After 2 hours, the reactor is vented, the polymer is filtered from the suspension, washed with
20 acetone and dried for 12 hours in a vacuum drying oven. This gives 38 g of polyethylene having an M_w of 297,000 and an M_w/M_n of 2.5 according to GPC.

Example 6:

25

The polymerization of Example 5 is repeated using high-purity ethylene, except that no TIBA was added. This gives 37 g of polyethylene having identical properties.

30 Example 7:

The polymerization of Example 5 is repeated, except that 2 ml of the catalyst solution are added and 100 ml of 1-hexene were first added to the reactor and 5 bar of
35 ethylene were subsequently added. After 30 minutes, the reactor is vented, the polymerization is stopped using methanol and the polymer is filtered from the suspension, washed with acetone and dried for 12 hours in a vacuum drying oven. This gives 25 g of an

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ethylene/1-hexene copolymer containing 5.2 mol% of hexene (according to ^{13}C -NMR) and having an M_w of 60,000 and an M_w/M_n of 2.6 according to GPC. The DSC melting point of the 2nd heating is 110°C.

5

Example 8:

A 1.5 dm³ autoclave, which was thoroughly flushed with ethene beforehand, is charged with 600 cm³ of an 85% strength by weight solution of norbornene in toluene. The solution is saturated with ethene by repeated pressurization with ethene (18 bar). A suspension of 2.28 mg of 4-(η^5 -cyclopentadienyl)-4,7,7-trimethyl-(η^5 -4,5,6,7-tetrahydroindenyl)Zr⁺CH₂CHCHCH₂B⁻(C₆F₅)₃ in 10 ml of toluene was added to the reactor thus prepared (in the case of hydrogen regulation, hydrogen can be injected at this point). Polymerization was carried out for one hour while stirring, with the ethene pressure being kept at 18 bar by metering in further amounts. After the end of the reaction time, the polymerization mixture was drained into a vessel and immediately introduced into 5 dm³ of acetone, the mixture was stirred for 10 min and the precipitated product was subsequently filtered off. The filter cake was washed alternately three times each with 10% strength hydrochloric acid and acetone. It was subsequently washed to neutrality with water, the residue was slurried in acetone and filtered again. The polymer thus purified was dried at 80°C for 15 hours in vacuo (0.2 bar). After drying, there were obtained 224 g of colorless polymer which had a glass transition temperature of 179°C, a viscosity number of 52 cm³/g, a tensile strength of 59 MPa and an elongation at break of 3.1%. The activity was 80.5 kg of polymer/h x mmol.

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Example 9

106 mg (0.385 mmol) of biscyclopentadienylzirconium-(η^4 -butadiene) were dissolved in toluene and admixed

- 20 -

with a solution of 186 mg (0.363 mmol) of $B(C_6F_5)_3$ in toluene. The formation of the catalyst can be recognized by the appearance of turbidity or of a precipitate.

In parallel thereto, a dry 16 dm³ reactor was flushed first with nitrogen and subsequently with propylene and then charged with 10 dm³ of liquid propylene. 15 cm³ of triisobutylaluminum (20% strength in hydrocarbon, 12 mmol) were then added to the reactor and the mixture was stirred at 30°C for 15 minutes. The catalyst suspension was subsequently added to the reactor, heated to the polymerization temperature of 70°C (4°C/min) and the polymerization system was held for 1 hour at 70°C by means of cooling. The polymerization was stopped by addition of 20 ml of isopropanol. The excess monomer was vented and residues of solvent were taken off in vacuo. This gave 850 g of liquid, atactic polypropylene. The catalyst activity was 8 kg of PP/(g of metallocene × h).

VN = 5 cm³/g, $M_w = 1500$ $M_w/M_n = 3.2$.

Example 10:

10 mg (17.9 mmol) of rac-dimethylsilanediyldis(2-methyl-4,5-benzo-1-indenyl)zirconium(η^4 -butadiene) were dissolved in 10 ml of toluene and admixed with 10 ml of a solution of 9.2 mg (18 mmol) of $B(C_6F_5)_3$ in toluene. The formation of the catalyst can be recognized by the appearance of turbidity or of a dark precipitate. The polymerization was carried out by a method similar to Example 9 at 70°C. The excess monomer was vented and the polymer powder was dried in vacuo. This gave 2500 g of isotactic polypropylene powder.

The catalyst activity was 250 kg of PP/(g of metallocene × h).

VN = 240 cm³/g, mp. = 148.7°C, $M_w = 298,000$, $M_w/M_n = 2.2$, $MFI_{(230/2.16)} = 3.2$ dg/min.

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Example 11:

The preparation of the catalyst suspension from Example 10 was repeated, except that 3 mg (4.8 mmol) of rac-di-methylsilanediylbis(2-methyl-4-phenyl-1-indenyl)-zirconium(η^4 -butadiene) dissolved in 10 cm³ of toluene were reacted with 2.5 mg (4.9 mmol) of B(C₆F₅)₃ dissolved in 10 cm³ of toluene. The polymerization was carried out at 60°C after adding the catalyst suspension to the reactor. The polymerization gave 2250 g of isotactic polypropylene powder.

The catalyst activity was 750 kg of PP/(g of metallocene × h).

VN = 620 cm³/g, mp. = 155°C, MFI_(230/5) = 0.35 dg/min.

Example 12:

The preparation of the catalyst suspension from Example 10 was repeated, except that 10 mg (21 mmol) of rac-di-methylsilanediylbis(2-methyl-1-indenyl)zirconium-(η^4 -butadiene) dissolved in 10 cm³ of toluene were reacted with 10.7 mg (21 mmol) of B(C₆F₅)₃ dissolved in 10 cm³ of toluene. The polymerization gave 1900 g of isotactic polypropylene powder. The catalyst activity was 190 kg of PP/(g of metallocene × h).

VN = 180 cm³/g, mp. = 145°C, $M_w = 192,000$, $M_w/M_n = 2.2$, MFI_(230/2.16) = 12 dg/min

Example 13:

The preparation of the catalyst suspension from Example 10 was repeated, except that 10 mg (20.2 mmol) of phenylmethylmethylenefluorenylcyclopentadienylzirconium-(η^4 -butadiene) dissolved in 10 cm³ of toluene were reacted with 10.7 mg (21 mmol) of B(C₆F₅)₃ dissolved in 10 cm³ of toluene. The polymerization gave 1100 g of syndiotactic polypropylene powder.

The catalyst activity was 110 kg of PP/(g of metallocene × h).

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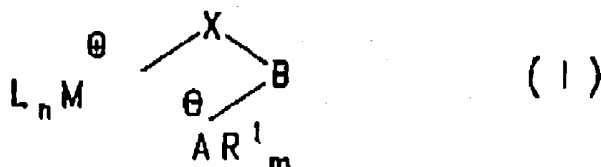
VN = 137 cm³/g, mp. = 133°C, $M_w = 122,000$ $M_w/M_n = 2.3$

Comparative Example:

- 5 The preparation of the catalyst suspension of Example 10 was repeated, except that 5 mg (11.1 mmol) of rac-dimethylsilanediyibis-1-indenylzirconium(η^4 -butadiene) dissolved in 10 cm³ of toluene were reacted with 5.7 mg (11.1 mmol) of B(C₆F₅)₃ dissolved in 10 cm³ of toluene.
- 10 The polymerization resulted in 2200 g of isotactic polypropylene powder.
The catalyst activity was 440 kg of PP/(g of metallocene x h).
VN = 52 cm³/g, mp. = 140°C, $M_w = 49,000$, $M_w/M_n = 2.2$
- 15 16.6 mg (40.7 mmol) of rac-dimethylsilanediyibis-1-indenylzirconiumdimethyl were dissolved in 10 cm³ of toluene and reacted with 21 mg (41 mmol) of B(C₆F₅)₃ dissolved in 10 cm³ of toluene. No turbidity or
- 20 precipitate formation can be observed. The catalyst solution is used for the polymerization as in Example 9. This resulted in 130 g of isotactic polypropylene powder.
The catalyst activity was 8 kg of PP/(g of metallocene x h).
- 25 VN = 67 cm³/g, mp. = 139.5°C, $M_w = 62,000$, $M_w/M_n = 2.1$

Claims

1. A zwitterionic transition metal compound of the formula I

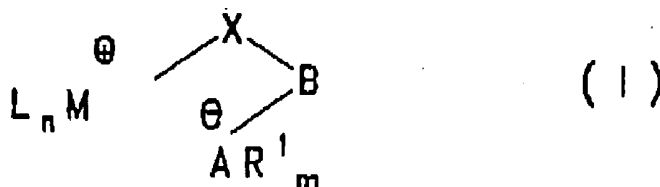


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where

- L are identical or different and are each a
n ligand or an electron donor, where two
radicals L can be linked to one another via a
bridge Z, n is equal to 1, 2, 3 or 4,
M is a metal of group IIIb, IVb, Vb or VIb of
the Periodic Table of the Elements,
X is a heteroatom or a hydrocarbon group,
B is a hydrocarbon group,
A is a metal atom of group Ib, IIb, IIIa, IIIb,
IVa, Va, Vb, VIb, VIIb or VIIIb,
R^I are identical or different and are each a
perhalogenated hydrocarbon radical, and m is
equal to 1, 2, 3, 4 or 5 and
if M is a metal of group IVb, n is 2.

2. A process for preparing a compound of the formula I,



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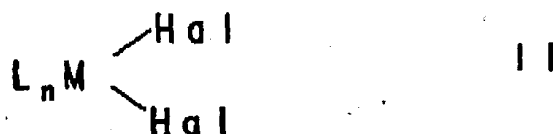
where

- L are identical or different and are each a
n ligand or an electron donor, where two
radicals L can be linked to one another via a
bridge Z, n is equal to 1, 2, 3 or 4,
M is a metal of group IIIb, IVb, Vb or VIb of

30

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the Periodic Table of the Elements,
 X is a heteroatom or a hydrocarbon group,
 B is a hydrocarbon group,
 A is a metal atom of group Ib, IIb, IIIa, IIIb,
 5 IVa, Va, Vb, VIb, VIIb or VIIIb,
 R¹ are identical or different and are each a
 perhalogenated hydrocarbon radical, and m is
 equal to 1, 2, 3, 4 or 5 and
 if M is a metal of group IVb, n is 2,
 10 which comprises reacting a compound of the formula
 II



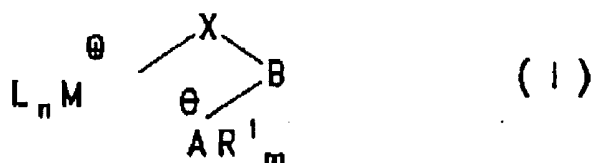
with a compound of the formula III



and reacting the reaction product with a compound
 of the formula AR¹_m, where L, n, M, X, B, A, R¹ and
 20 m in the formulae II, III and AR¹_m are as defined
 for the formula I and Hal is a halogen.

3. A process for preparing an olefin polymer by poly-
 merization or copolymerization of at least one
 olefin in the presence of a catalyst comprising at
 25 least one transition metal compound of the formula
 I,

- 25 -



where

- L are identical or different and are each a
 n ligand or an electron donor, where two
 radicals L can be linked to one another via a
 bridge Z, n is equal to 1, 2, 3 or 4,
 M is a metal of group IIb, IVb, Vb or VIb of
 the Periodic Table of the Elements,
 X is a heteroatom or a hydrocarbon group,
 B is a hydrocarbon group,
 A is a metal atom of group Ib, IIb, IIIa, IIIb,
 IVa, Va, Vb, VIb, VIIb or VIIIb,
 R^I are identical or different and are each a
 perhalogenated hydrocarbon radical, and m is
 equal to 1, 2, 3, 4 or 5, and
 if M is a metal of group IVb, n is 2.

HOE 94/F 160

ABSTRACT

The present invention relates to zwitterionic neutral transition metal compounds. The compounds are suitable
5 as catalyst components for the polymerization of olefins.

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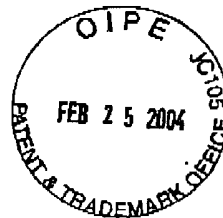
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Documents Filed:

Transmittal Letter (1 page)

Certified translation of German application P44 20 456.6



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